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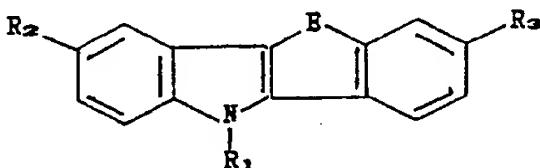
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54 Conductor polymers usable in the construction of completely dry batteries.

57 Conductor polymers prepared by anodic oxidation of compounds of general formula (I)



(I)

in which E = O, S, Se;

R₁ = H or a saturated or unsaturated alkyl radical with double bonds in the vinyl or allyl position with respect to the nitrogen;

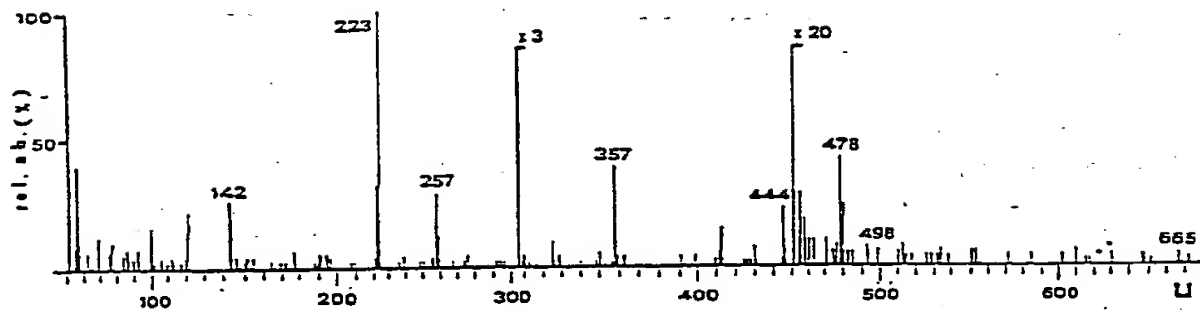
R₂, R₃ = H or methyl radicals.

These polymers have a cross-linked structure with intermonomer bonds in which possible nitrogen-bonded vinyl groups and the aromatic rings are involved, and delocalized positive charges in the chain neutralized by counter-ions such as Cl⁻, BF₄⁻, ClO₄⁻ or PF₆⁻.

Said polymers can be used in the construction of rechargeable batteries of completely solid state.

EP 0 346 822 A1

FIG. 1



CONDUCTOR POLYMERS USABLE IN THE CONSTRUCTION OF COMPLETELY DRY BATTERIES

Field of the invention

This invention relates to organic polymers having delocalized positive charges in the chain neutralized
 5 by inorganic counter-ions, and suitable for use both as electrolytes and as electrode materials in the construction of completely dry batteries.

Prior art

10 Numerous conductor polymers and their relative preparation methods are known, these being based on electrochemical polymerization in the presence of an auxiliary electrolyte.

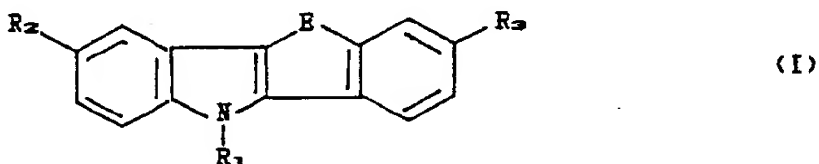
For example, a method for preparing polypyrrole is described in Japanese patent 131,104 (1986); a method for preparing polythiophene is described in Japanese patent 62,521 (1986); the preparation of
 15 polymers of aminochrysene, aminofluoranthene, aminophenanthrene, naphthylamine, 2-aminobenzimidazole and 2-aminobenzothiazole is described in Japanese patent 219,228 (1985).

Said polymers have prospective applications of considerable importance as they can be used for battery electrodes, electrochemical sensors, electrochromic devices and other applications.

20 However, when used as electrodes, these polymers present self-discharge problems.

Summary of the invention

We have now discovered new conductor polymers prepared by anodic oxidation of compounds of
 25 general formula (I)



in which E = O, S, Se;

35 R₁ = H or a saturated or unsaturated alkyl radical with double bonds in the vinyl or allyl position with respect to the nitrogen;

R₂, R₃ = H or methyl radicals,

and having a cross-linked structure with intermonomer bonds in which possible nitrogen-bonded vinyl groups and the aromatic rings are involved, and delocalized positive charges in the chain neutralized by
 40 counter-ions such as Cl⁻, BF₄⁻, ClO₄⁻ or PF₆⁻.

The present invention also relates to the use of said polymers both as electrolytes as electrode materials for the construction of completely dry batteries.

These polymers are not subject to significant self-discharge phenomena when used as electrolytes for the construction of completely dry batteries.

45 They are prepared by electrochemical polymerization of (I) by anodic oxidation in an organic solvent in the presence of a transport electrolyte which provides the counter-ion.

Detailed description of the invention

50 The characteristics of the polymers according to the present invention and of their preparation method plus their possible applications as battery electrolytes will be illustrated in detail in the following description.

The monomer (I) is prepared by known methods, for example a monomer (I) can be prepared by N-vinylation of thionaphthene indole applying the method used for the N-vinylation of carbazole described by

G.R. Clemo, W.H. Perkin in J. Chem. Soc. Trans., 1924, 125, 1804. The product obtained can be purified chromatographically and characterized by NMR and MS.

The monomer (I) is dissolved in an organic solvent in a quantity such as to obtain a concentration of between $5 \cdot 10^{-3}$ moles/litre and its solubility in the solvent itself. Suitable solvents are aprotic solvents such as CH_2Cl_2 , CH_3CN , $\text{C}_6\text{H}_5\text{CN}$ and dimethylformamide.

The preferred solvent is CH_2Cl_2 .

A transport electrolyte represented generically by MX in which M is Li , Na , K , NR_4 where R_4 is C_1 - C_4 alkyl and X is Cl , BF_4 , ClO_4 or PF_6 is added to the solution.

The preferred transport electrolyte is NBu_4ClO_4 .

The transport electrolyte concentration in the solution is between 0.01 and 1 mole/l and preferably between 0.08 and 0.12 moles/l.

The method is preferably conducted in an anhydrous medium, however lifted quantities of water of up to 10^{-2} moles/l do not negatively influence the process.

The oxygen has to be completely removed from the solution, this being preferably done by bubbling an inert gas through such as argon or nitrogen, and in addition the electrochemical process must be conducted in an inert gas atmosphere.

The electrodes of the electrolytic cell used for the electrochemical polymerization are of metal or metal oxide, and preferably Pt , Au , steel or SnO_2 . In the cell the cathode compartment is separated from the anode compartment by porous diaphragm means.

The cell is advantageously provided with a saturated calomel reference electrode.

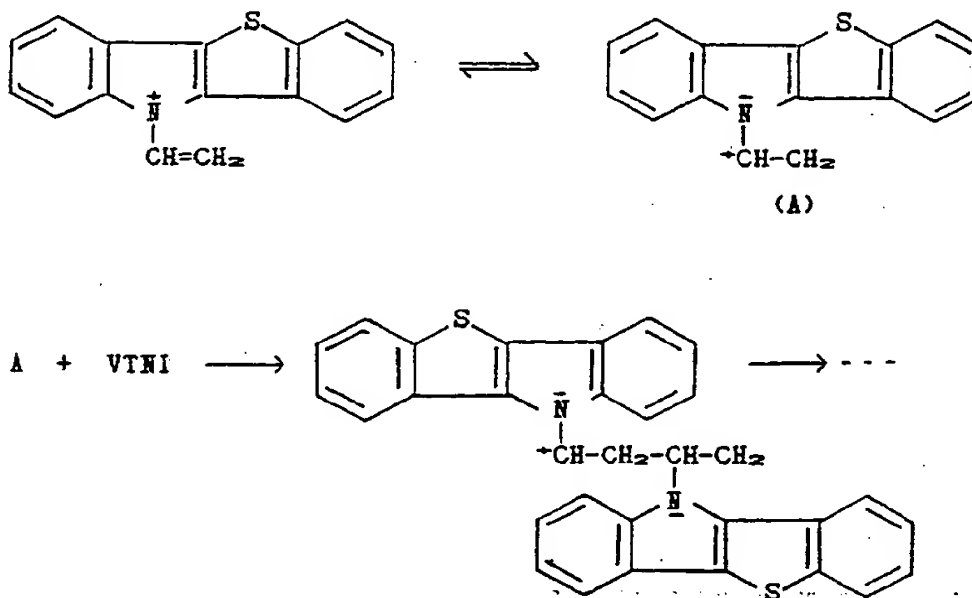
The electrochemical polymerization is conducted at a constant potential of between +1 and +3.5 V and preferably between +1.2 and +1.3 V with respect to the saturated calomel electrode.

However it can also be conducted at constant current density, with the current density between 0.6 and 3 mA/cm^2 and a potential difference between the anode and cathode of about 100 V.

The polymerization is conducted at a temperature of between 10 and 40°C .

At the anode a black, oxidised, insoluble polymer deposit is obtained, and is washed with solvent of the type used in the preparation, and then dried. Chemical, physico-chemical and electrical characterization tests are carried out on the product, together with applicational tests regarding its use as electrolytic material for batteries.

On elementary chemical analysis the polymer of the present invention obtained using R-vinylthionaphthene-indole (VTNI) as monomer and NBu_4ClO_4 as transport electrolyte consists of repetitive units of formula $[\text{p}(\text{VTNI})^y \cdot y\text{ClO}_4^- + z\text{H}_2\text{O}]_n$ in which there is a difference in hydrogen content with respect to the theoretical formula $\text{C}_{16}\text{H}_{11}\text{SN}$, due to bonds between the aromatic rings, whereas the bonds are prevalently on the side chain in accordance with the scheme:



The mass spectrum for the product, shown in Figure 1, indicates peaks relative to high-mass ions

congruent with a polymer substance.

The results of the mass spectrometry measurements are given in Table 1, which shows the structure of some of the more significant ionic species.

These structures confirm that the polymerization takes place with the formation of bonds both between the vinyl groups and between the benzene rings.

Electrical conductivity tests were carried out on the polymer obtained, using the method described in G. Casalbore-Miceli, G. Beggiato, S. Dadio, P.G. Di Marco, S.S. Emmi, G. Giro, J. Appl. Electrochem. 17 (1987) 1111.

In the various examined samples the specific conductivity is between 0.97 and $1.1 \times 10^{-5} \text{ ohm}^{-1}\text{cm}^{-1}$. The polymers according to the invention were used with surprising results in the construction of solid rechargeable batteries in which the same polymers were shown to be able to operate both as electrolytes and as electrode materials. Consequently this application also constitutes a subject of the present invention.

The battery according to the present invention consists of the following elements all in the solid state:

(-) $\text{Me}_1 // [\text{p}(\text{I})^y \cdot y\text{X}^- + z\text{H}_2\text{O}]_n // \text{Me}_2 (+)$

in which Me_1 is an oxidisable metal such as Zn, Cu, Fe and preferably Zn, Me_2 is a noble metal such as Au, Pt or metallic oxide, $\text{p}(\text{I})$ is the polymer according to the invention, X^- is the counter-ion and z is a number between 1 and 2.

When Me_1 is Zn and Me_2 is Au, the battery can be charged to give an anodic potential of between 1.5 and 5 V at the electrode Me_2 with respect to the electrode Me_1 .

The electrode processes can be schematised in the following manner:

$\text{Me}_1^{++} + 2\text{e}^- \longrightarrow \text{Me}_1$ (reaction at cathode)

$2\text{P} - 2\text{e}^- \longrightarrow 2\text{P}^+$ (reaction at anode)

where P^+ represents a delocalized positive site in the polymer chain.

When Me_1 is Zn and Me_2 is Au, the battery has an open circuit voltage of about 0.85 V.

When the element operates as a current generator (battery discharge), the following reactions occur:

Me_2 (positive pole) $2\text{e}^- + 2\text{P}^+ \longrightarrow 2\text{P}$

Me_1 (negative pole) $\text{Me}_1 - 2\text{e}^- \longrightarrow \text{Me}_1^{++}$

These reactions are evidenced by the following observations:

- Me_1 is the negative pole of the battery;
- after various cycles, whereas the Me_2 /polymer interface does not appear modified, the Me_1 /polymer interface appears pitted with the formation of an unidentified solid substance;
- the battery voltage does not appear significantly modified when using an Au or Pt electrode for Me_2 , whereas if a Zn, Cu or Fe electrode is used for Me_1 the battery voltage varies significantly;
- the voltage agrees well with the theoretical value for the aforesaid electrode reactions.

In the battery according to the invention the polymer therefore acts both as the electrode material and as the solid electrolyte. In this respect, during operation of the battery as a generator, the voltage measured immediately after opening the circuit is less than the value which is gradually established on leaving the circuit open, whereas during operation of the battery as an electrolyzer (charge stage), the voltage measured immediately after opening the circuit is higher than that which is gradually established on leaving the circuit open.

There is thus a slow diffusion of the charges in the electrolyte and a polarization overvoltage at the electrodes. This has also been demonstrated by the difference in the specific resistance of the polymer when measured in an alternating field and in a direct field.

The diffusion overvoltage is therefore the "slow stage" in the battery operation. In this respect, a large variation in external resistance does not significantly influence the delivered current. Significant variations are obtained for loads of the order of 100 kohm.

The battery according to the invention is particularly advantageous because of the following characteristics:

- battery totally of solid state;
- easy construction;
- not subject to substantial self-discharge phenomena;
- rechargeable for a large number of cycles;
- light in weight;
- non-polluting constituent material;
- possibility of recovering the electrode materials;
- possibility of assembling several elements to obtain high voltage;
- protection from short-circuiting by internal polarization;
- possibility of varying the internal resistance by dispersing salts of the electrode metal in the polymer

electrolyte or subjecting the battery to preliminary cycles.

Said battery can be used for example in watches, calculators, cardiac stimulators, microelectronics and portable instruments generally.

The following examples are given by way of non-limiting illustration of the invention.

EXAMPLE 1

A solution of R-vinyl-thionaphthene-indole (VTNI) and tetrabutylammonium perchlorate (TBAP) in methylene chloride was fed into an electrolytic cell of capacity 4 ml.

The VTNI had been purified by chromatography and characterised by NMR and MS; the TBAP (Fluka purum) had been recrystallized from methanol and the methylene chloride had been distilled from P_2O_5 in a nitrogen atmosphere.

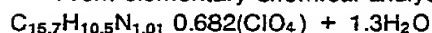
The VTNI concentration in the solution was 5×10^{-2} M and the TBAP concentration was 0.1 M.

The electrolytic cell was provided with Pt electrodes, of which the anode was in the form of a platinum plate of area 1 cm^2 . The cathodic compartment containing a platinum spiral was separated from the anodic compartment by a sintered glass diaphragm. The cell was also provided with a saturated calomel reference electrode.

The solution was degassed by bubbling nitrogen through in order to completely remove the oxygen, after which polymerization was commenced by electrochemical oxidation operating with a potential difference of 1.2 V. The polymerization was conducted at 22°C in a nitrogen atmosphere.

The polymer deposited at the anode in the form of a black solid deposit with a yield of 76%.

From elementary chemical analysis the polymer was found to have the following formula:



The mass spectrum was as shown in Figure 1. The specific conductivity was $1.1 \times 10^{-5} \text{ ohm}^{-1}\text{cm}^{-1}$.

EXAMPLE 2

The polymer obtained by operating in accordance with Example 1 was used to construct a rechargeable battery formed from the following elements:

(-)Zn//poly-VTNI $^+$ (ClO_4^-)//Au (+)

all in the solid state and with the following constructional characteristics:

- electrode diameter (Au and Zn).....	0.5 cm
- electrode area.....	0.196 cm^2
- thickness of polymer layer (oxidised poly-VTNI powder compressed to 2 ton.).....	661 microns
- weight of polymer (density about 1).....	13 mg
- maximum current 20 μA ; average current 2-3 μA (load = 1000 Ω)	

The battery was charged by providing a potential of 5 V at the Au anode with respect to the Zn, to obtain an open-circuit battery voltage of slightly less than 1 V. This voltage corresponds to the free energy of the following reactions taking place during the discharge stage:

Au (positive pole) $2e^- + 2P^+ \longrightarrow 2P$ ($E^\circ = -0.1$) (saturated calomel electrode)

Zn (negative pole) $Zn - 2e^- \longrightarrow Zn^{++}$ ($E^\circ = -1 \text{ V}$ in aqueous solution) (saturated calomel electrode)

The ratio of delivered charge to supplied charge is close to 1.

The battery internal resistance varies with the number of cycles or on dispersing a Zn salt in the polymer electrode (2 MO-1600 Ω).

The theoretical capacity depends on the extent of polymer oxidation and can range from 55 to 80 Ah/kg of polymer.

EXAMPLE 3

A battery was constructed consisting of two elements as described in Example 2 but with the positive pole formed of platinum instead of gold. The electrodes were 1 cm^2 .

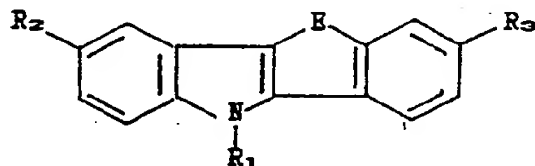
The voltage was practically additive (1.9 V), the maximum current delivered was 400 μ A and the average current 30-40 μ A.

TABLE 1: RESULTS OF MASS SPECTROMETRY MEASUREMENTS ON POLY VINI'S

m/z	empirical formula	structure formula	m/z	empirical formula	structure formula
665	$C_{42}H_{22}N_3S_3$		325	$C_{22}H_{16}NS$	
498	$C_{32}H_{22}N_2S_2$		257	$C_{18}H_{13}N_2$ or $C_{18}H_{29}$	
478	$C_{31}H_{18}NS_2$ or $C_{33}H_{38}NS$		223	$C_{14}H_9NS$	
444	$C_{28}H_{10}N_2S_2$		142	$C_{10}H_8N$	
412	$C_{28}H_{22}NS_2$ or $C_{28}H_{30}NS$		121	C_7H_5S or C_9H_{13}	
387	$C_{22}H_{18}NS_2$ or $C_{24}H_{23}NS$		120	$C_8H_{10}N$	
			93	C_6H_7N	
			78	C_6H_8	

Claims

1. Conductor polymers usable in the construction of completely dry batteries, prepared by anodic oxidation of compounds of general formula (I)



(I)

in which E = O, S, Se;

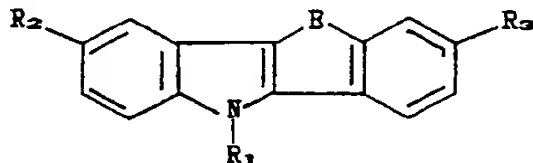
R₁ = H or a saturated or unsaturated alkyl radical with double bonds in the vinyl or allyl position with respect to the nitrogen;

R₂, R₃ = H or methyl radicals,

and having a cross-linked structure with intermonomer bonds in which possible nitrogen-bonded vinyl groups and the aromatic rings are involved, and delocalized positive charges in the chain neutralized by counter-ions such as Cl⁻, BF₄⁻, ClO₄⁻, PF₆⁻.

2. Polymers as claimed in claim 1, characterised by having an electrical conductivity of between 0.9 and $1.1 \times 10^{-5} \text{ } \Omega^{-1}\text{cm}^{-1}$.

3. A method for preparing conductor polymers usable in the construction of completely dry batteries, prepared by anodic oxidation of compounds of general formula (I)



(I)

in which E = O, S, Se;

R₁ = H or a saturated or unsaturated alkyl radical with double bonds in the vinyl or allyl position with respect to the nitrogen;

R₂, R₃ = H or methyl radicals,

and having a cross-linked structure with intermonomer bonds in which possible nitrogen-bonded vinyl groups and the aromatic rings are involved, and delocalized positive charges in the chain neutralized by counter-ions such as Cl⁻, BF₄⁻, ClO₄⁻ or PF₆⁻, characterised by using electrochemical oxidation to polymerize a compound (I) dissolved in a medium consisting of an aprotic organic solvent in the presence of a transport electrolyte able to supply said counter-ion.

4. A method as claimed in claim 3, characterised in that said organic solvent is CH₂Cl₂, CH₃CN, C₆H₅CN or dimethylformamide, and is preferably CH₂Cl₂.

5. A method as claimed in claim 3, characterised in that said transport electrolyte is a compound MX in which M is Li, Na, K or NR₄ where R₄ is C₁-C₄ alkyl, and X is ClO₄, Cl, BF₄ or PF₆.

6. A method as claimed in claim 5, characterised in that said transport electrolyte is NBu₄ClO₄.

7. A method as claimed in claim 3, characterised in that the compound (I) is dissolved in said organic solvent in a quantity such as to obtain a concentration of between 5×10^{-3} moles/l and the actual solubility of (I) in the solvent.

8. A method as claimed in claim 3, characterised in that said transport electrolyte is dissolved in said organic solvent in such a quantity as to obtain a concentration of between 0.01 and 1 mole/l and preferably between 0.08 and 0.12 moles/l.

9. A method as claimed in claim 3, characterised by operating in a medium which is anhydrous or contains a quantity of water not exceeding 10^{-2} moles/l.

10. A method as claimed in claim 3, characterised by operating in an oxygen-free medium in an atmosphere of inert gas.

11. A method as claimed in claim 3, characterised in that said anodic oxidation is conducted in an electrolytic cell provided with electrodes of Pt, Au, Ni, steel or SnO₂.

12. A method as claimed in claim 3, characterised in that said anodic oxidation is conducted at constant potential, with an anodic potential of between 1 V and 3.5 V (with respect to saturated calomel).

13. A method as claimed in claim 3, characterised in that said anodic oxidation is conducted at a constant current density of between 0.6 and 3 mA/cm² and a potential difference between the anode and cathode of about 100 V.

14. A method as claimed in claim 3, characterised in that said anodic oxidation is conducted at a temperature of between 10 and 40 °C.

15. A rechargeable solid-state battery comprising as electrolyte a polymer as defined in claims 1 and 2, and consisting of the elements:

(-) Me₁/[p(l)]^y yX⁻ + zH₂O]/Me₂(+)

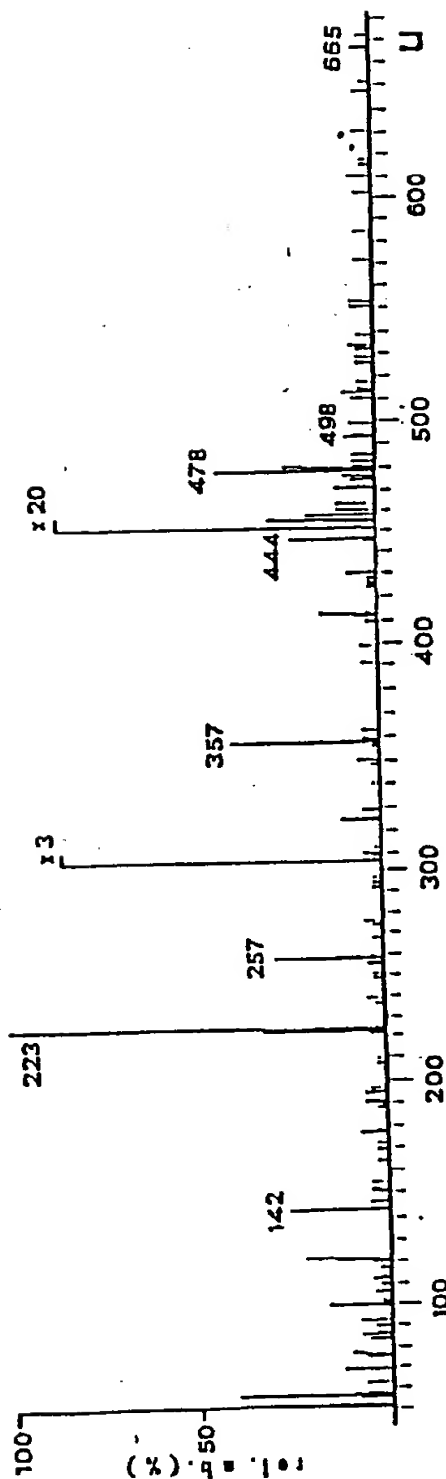
in which Me₁ is an oxidisable metal such as Zn, Cu or Fe, and Me₂ is a noble metal such as Au, Pt or metallic oxide, p(l) is the polymer according to the invention, X is ClO₄, Cl, BF₄ or PF₆ and z is a number between 1 and 2.

16. A battery as claimed in claim 15, characterised in that Me₁ is Zn and Me₂ is Au.

17. A battery as claimed in claim 16, characterised by being charged by applying an anodic potential of between 1.5 and 5 V to the Au electrode with respect to the Zn electrode.

18. A battery as claimed in claim 17, characterised by having an open-circuit voltage of about 0.85 V.

FIG. 1





DOCUMENTS CONSIDERED TO BE RELEVANT			EP 89110664.3
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	JOURNAL OF APPLIED ELECTRO-CHEMISTRY, vol. 17, no. 1, January 1987 G.CASALBORE MICELI et al. "Electrochemical polymerization of thionaphtene-indole" pages 1111-1117 * Abstract; introduction; experimental details *	1,3-6, 11,14	H 01 M 10/36 H 01 B 1/12 C 25 B
X	SYNTHETIC METALS, vol. 15, 1986, Lausanne G.CASALBORE MICELI et al. "Electrochemical polymerization of N-Allyl-thionaphtene-indole" pages 1-7 * Abstract; introduction; experimental *	1,3-6, 11,14	
A	US - A - 4 520 086 (SKOTHEIM) * Abstract *	15	TECHNICAL FIELDS SEARCHED (Int. Cl.4)
A	US - A - 4 182 798 (SKARSTAD) * Column 1, lines 7-45 *	15	H 01 B H 01 M C 25 B
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 19-09-1989	Examiner LUX
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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